10.40 Thermodynamics **Fall 2003**
Exam 2

Problem 2

2. (10 points) Imagine a lattice consisting of *10000* sites filled with *3000* indistinguishable particles at temperature T. Only one particle can reside at each lattice site and there is no energy of interaction between particles of any type. The initial state is such that the 3000 particles occupy 30% of the lattice volume separated by a partition from the rest of the lattice. Compute the change in $\underline{G}$ from the initial state to a final equilibrium state.

Solution:

To compute the change in $\underline{G}$ for this process, we begin by noting that :
$\underline{G} = \underline{H} - T\underline{S}$

However, since there is no energy of interaction between particles of any type (ie. there is no bond breakage and/or formation), the enthalpy of the final state will be the same as the initial state. Therefore, for the constant temperature process:

$$\Delta\underline{G} = \underline{G}_f - \underline{G}_i = \underbrace{\left(\underline{H}_f - \underline{H}_i\right)}_{=0} - T\left(\underline{S}_f - \underline{S}_i\right)$$

Since the energy of all states is the same, we can use the definition of entropy from the microcanonical ($\underline{E}$, $\underline{V}$, N) ensemble. For the indistinguishable particles for which only one particle can reside at each site, combinatorics tells us that:

$$\underline{S} = k\ \ln\Omega = k\ \ln\left(\frac{M!}{N!(M-N)!}\right)$$ where M = # lattice sites and N = # particles

For the initial case, there is only one possible configuration (3000 particles in 3000 lattice sites), so $\Omega = 1$ and $\underline{S}_i = 0$. For the final state, we use Stirling's approximation: $\ln N! = N\ln N - N$:

$$\underline{S}_f = k\ \ln\left(\frac{M!}{N!(M-N)!}\right) = k\left[M\ \ln M - N\ \ln N - (M-N)\ln\ (M-N)\right]$$

$$\underline{S}_f = 6109k$$

Plugging in values, we find that:

$$\Delta\underline{G} = \underline{G}_f - \underline{G}_i = 0 - kT(6109 - 0)$$

$$\underline{\Delta\underline{G} = -6109\ kT}\ .$$

The following alternative route to the solution was used by several students:

$$\Delta \underline{G} = \underline{G}_f - \underline{G}_i = \left(\underline{A}_f - \underline{A}_i\right) + T \underbrace{\left(P\underline{V}_f - P\underline{V}_i\right)}_{=0 \text{ since } P=0 \text{ for lattice gas}}$$

$$\underline{A} = -kT \ln Q_N$$

$$Q_N = \Omega \qquad \text{since } E_i = \text{constant}$$

$$\underline{A}_i = 0 \qquad \underline{A}_f = -kT \ln\left(\frac{M!}{N!\left(M-N\right)!}\right) = 6109kT$$

$$\Delta \underline{G} = \underline{G}_f - \underline{G}_i = -kT\left(6109 - 0\right)$$

$$\underline{\Delta \underline{G} = -6109\ kT}$$